

# Nuclear magnetic resonance and relaxation in liquid Ga and GaSb<sup>†</sup>

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Measurements of the Knight shift and nuclear-spin-lattice relaxation rate of <sup>69</sup>Ga and <sup>71</sup>Ga in liquid Ga, and <sup>69</sup>Ga, <sup>71</sup>Ga, <sup>121</sup>Sb, and <sup>123</sup>Sb in liquid GaSb are reported over temperatures ranging from the supercooled regions up to 1250–1373 K. From the Knight shifts of <sup>121</sup>Sb and <sup>123</sup>Sb in GaSb, the hyperfine structure anomaly of the Sb isotopes is measured. An attempt to relate the observed quadrupolar relaxation rates to existing theories based on ionic diffusion models indicates that the latter are not adequate to explain all aspects of the observations. In the case of liquid GaSb, the quadrupolar coupling was found to be much stronger for Sb than for Ga. It is proposed that this is caused by an effect of alloying on the antishielding factors.

## I. INTRODUCTION

The technique of pulsed nuclear magnetic resonance is recognized as a useful tool for providing information on the electronic structure of liquid metals. Measurements of the Knight shift ( $K$ ) and the contribution of magnetic hyperfine interactions to the nuclear-spin-lattice relaxation rate  $T_1^{-1}$  provide information about the static and dynamic magnetic fields experienced by a nucleus in a liquid metal. In addition to the magnetic interaction, some characteristics of the dynamic electric field gradients in the liquid may also be obtained for nuclei which possess electric quadrupole moments, since the quadrupolar interaction may make an observable contribution to spin-lattice relaxation.

In this work, experimental measurements of the Knight shift and spin-lattice relaxation time are reported for <sup>69</sup>Ga and <sup>71</sup>Ga in liquid Ga and for <sup>69</sup>Ga, <sup>71</sup>Ga, <sup>121</sup>Sb, and <sup>123</sup>Sb in liquid GaSb. A temperature range extending from the respective supercooled regions to 1250–1373 K is covered, and several resonance frequencies are employed.

The main purpose of this work is to evaluate the relative importance of the various mechanisms which can contribute to  $T_1$  and  $K$  in these systems. Since the temperature dependence is an important parameter for determining the mechanism responsible for the relaxation, we have covered a wide temperature range. Also, we have placed heavy emphasis on achieving high accuracy, as the quadrupolar contribution to relaxation often is much smaller than the magnetic contribution in liquid metals. The possibility of making measurements of two isotopes is particularly important for spin-lattice relaxation studies since this permits unambiguous separation of competing magnetic dipole and electric quadrupole relaxation processes.

An important motivation of this work has been the need for further study of the magnitude and temperature dependence of the quadrupolar contribution to the relaxation rate in liquid metals. The

source of this contribution has been attributed to the diffusion of ions.<sup>1–10</sup> Theoretical treatments based on this interpretation have been given by Sholl and others.<sup>11,12</sup> We have found that this model does not predict correctly the temperature dependence of the quadrupolar rate over all temperatures. A more recent approach by Warren<sup>13</sup> gives excellent agreement with the magnitude of quadrupolar relaxation near the melting point in liquid Ga, but requires measurements of liquid-structure factors over a wide temperature range before its prediction for the temperature dependence can be tested.

In the intermetallic compound liquid GaSb, large differences were found in the quadrupolar coupling of the Ga and Sb ions. It is proposed that this is due to an effect of alloying on the antishielding factors. The details of this argument are given in Sec. III C.

## II. EXPERIMENTAL DETAILS AND RESULTS

### A. Apparatus, measurements, and samples

The spin-lattice relaxation times and Knight shifts were measured using a pulsed spectrometer similar to one described by Clark.<sup>14</sup> Absorption line shapes were obtained by sweeping the field through resonance and recording the free-induction-decay (FID) signal with a boxcar integrator.<sup>15</sup> Values of the Knight shift were obtained by comparing the resonance frequency of the desired nucleus in the sample and in an aqueous solution (reference sample) with the frequency ( $\nu_D$ ) of the deuteron resonance (D<sub>2</sub>O doped with GdCl<sub>3</sub>) in the same magnetic field. The frequency of the deuteron resonance was measured with a Robinson-type oscillator.<sup>16</sup> In the case of Sb, the reference sample was dilute HSbF<sub>6</sub> (we used the published values of  $\nu_{Sb}/\nu_D$  as measured by Warren and Clark).<sup>17</sup> For Ga, the reference sample was dilute GaCl<sub>3</sub>. Our measurements of  $\nu_{Ga}/\nu_D$  are in complete agreement with those of Valic.<sup>18</sup> The accuracy of the shift measurements was limited mainly by the error in setting the rela-

tive phase between the NMR and rf oscillator reference signals to  $0^\circ$ . The experimental errors in the Knight shifts were  $\pm 0.0005\%$  in liquid-Ga metal and  $\pm 0.001\%$  for  $^{69}\text{Ga}$  and  $^{121,123}\text{Sb}$  in liquid GaSb.

Most spin-lattice relaxation times were measured using a conventional  $180^\circ$ - $90^\circ$  pulse sequence.<sup>19</sup> The conventional technique was not adequate, however, when an attempt was made to measure the  $T_1$ 's of  $^{69}\text{Ga}$  and  $^{121}\text{Sb}$  in liquid GaSb. The reason for this is that the  $^{69}\text{Ga}$  and  $^{121}\text{Sb}$  resonances in the liquid state are separated by only about 9 G at 10 kG. When an attempt is made to measure the amplitude of the on-resonance FID of one of the nuclear species, the off-resonance FID of the neighboring resonance interferes. Therefore, a new method was devised which resulted in almost total elimination of the interference. This method is discussed in detail elsewhere.<sup>20</sup> In all cases the relaxation proved to be exponential with a single decay time  $T_1$ .

The accuracy of the  $T_1$  measurements in liquid GaSb was  $\pm 3\%$  at the lower temperatures and about 4-5% at the highest temperatures. The  $T_1$  measurements in liquid Ga were accurate to 1-2% at the lower temperatures and about  $\pm 2\%$  at the highest temperatures.

The basic design of the furnace used for the high-temperature NMR experiments is an adaptation of a design by Warren and Clark<sup>21</sup> that takes advantage of the simpler configuration of the single coil<sup>20,22</sup> as opposed to cross coils and Pt-10-at.-%-Rh heaters for more reliable high-temperature operation. The accuracy of the temperature measurements was typically  $\pm 0.02\%$ . The stability obtained at 1000 K is  $\pm 0.5$  K with the rf pulses operating. The furnace and probe are described in detail elsewhere.<sup>20</sup>

The GaSb samples used in these experiments were prepared from a single crystal supplied by Cominco American.<sup>23</sup> It was crushed and sieved to obtain particle sizes in the range 100-325 mesh. The crushed GaSb was then mixed with an equal amount by volume of quartz powder of comparable particle dimensions to ensure that in the liquid state the sample would approximate a dispersion of particles small enough to permit nearly complete penetration of the rf magnetic field.

The Ga metal was obtained in ingot form from the Research Inorganic Chemical Co.<sup>24</sup> The specified purity of the Ga was 99.99%. The powdered samples were prepared by melting the metal in mineral oil and stirring with a blender. The oil was then cooled below the melting point of the particles and the particles were allowed to settle out of the oil. These particles were then washed with benzene and mixed with an equal amount of quartz powder. The particle sizes were approximately 400 mesh.

## B. Experimental results

### 1. Gallium

Since there is a large static quadrupolar interaction in solid Ga, our powdered samples did not show any NMR signals in the solid phase. In the liquid, however, rapid thermal motion averages the static quadrupolar interaction to zero, yielding a strong nuclear resonance signal for each isotope. Measurements of the  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  Knight shift in liquid Ga were made from 300 to 1250 K at 18.75 MHz. Also, measurements of the  $^{69}\text{Ga}$  Knight shift in supercooled Ga were made from 230 to 300 K at 18.75 MHz (the melting point of Ga is 303 K). These data are shown in Fig. 1. The observed values of  $K(^{69}\text{Ga})$  and  $K(^{71}\text{Ga})$  decrease with increasing temperature according to the empirical relationships:

$$T > 300 \text{ K,}$$

$$K(^{69,71}\text{Ga}) = [(0.4528 \pm 0.0005) - 3.26 \times 10^{-5}(T - 300) + 8.17 \times 10^{-9}(T - 300)^2]\%$$

$$T < 300 \text{ K (supercooled),}$$

$$K(^{69}\text{Ga}) = [(0.4528 \pm 0.0002) - 3.26 \times 10^{-5}(T - 300) - 1.25 \times 10^{-7}(T - 300)^2]\%$$

Our measurements may be compared with the earlier measurements of Cornell,<sup>2</sup> who measured  $K(^{71}\text{Ga})$  in liquid Ga in the temperature range 300-740 K, the measurements of Valic,<sup>18</sup> who measured  $K(^{71}\text{Ga})$  in liquid Ga in the temperature range 303-331 K, the measurements of Suzuki and Uemura,<sup>25</sup> who measured the temperature dependence of  $K(^{69}\text{Ga})$  from 195 to 325 K, and the measurements

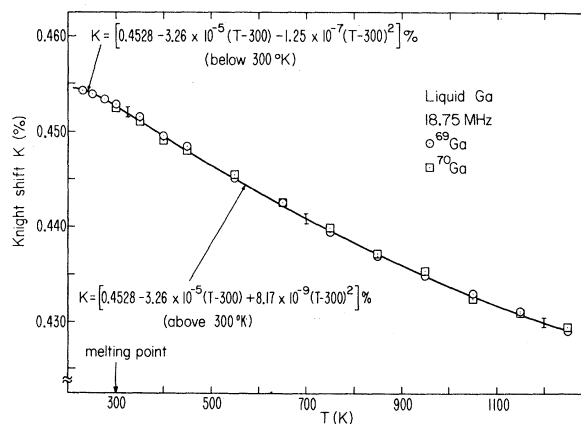


FIG. 1. Experimental Knight shifts  $K(^{69}\text{Ga})$  and  $K(^{71}\text{Ga})$  for  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  in liquid gallium as a function of temperature. Representative errors are indicated by the flags. Note the discontinuity in the vertical scale. The solid line is given by the empirical relationships shown on the figure.

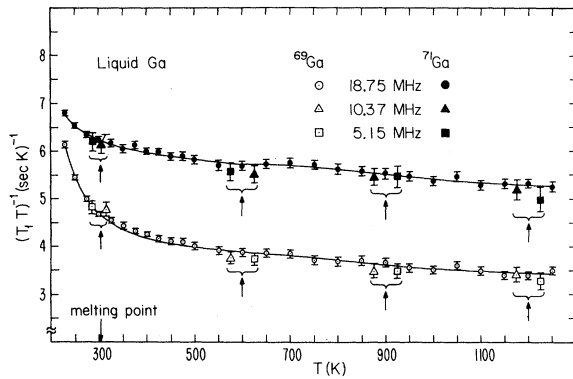


FIG. 2. Experimental values of  $(T_1 T)^{-1}$  for  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  in liquid gallium as a function of temperature. Data points within a given grouping were all taken at the temperature indicated by the corresponding arrow. The solid line represents our fit to the data.

of Hechtfisher *et al.*,<sup>26</sup> who measured the temperature dependence of  $K(^{71}\text{Ga})$  in a bulk sample between 285 and 327 K. Our data agree with those of Cornell if a small uniform shift is applied. This disagreement may be due to the use of a different reference from Cornell's (undescribed). On the other hand, there is complete agreement with the measurements of Valic. Our data also agree with those of Suzuki and Uemura, and with Hechtfisher *et al.*, within experimental error. However, all of the above authors conclude that  $K(\text{Ga})$  above 300 K varies linearly with the temperature, whereas in the wider temperature range that we have covered it is also necessary to include a term quadratic in the temperature.

Measurements of the  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  nuclear relaxation rates in liquid Ga were made in the temperature range 230–1250 K at 18.75 MHz. As in the case of the Knight shifts, measurements below the melting point (303 K) were possible owing to supercooling. The data are plotted in the form  $(T_1 T)^{-1}$  vs  $T$  in Fig. 2. In addition to the measurements at 18.75 MHz (circles on Fig. 2)  $T_1$  measurements at several representative temperatures were also made at 10.37 MHz (triangles on Fig. 2) and at 5.15 MHz (squares in Fig. 2) to see if there is any frequency dependence to  $T_1$ . None was observed. The  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  data exhibit a large decrease of  $(T_1 T)^{-1}$  with increasing temperature in the supercooled region (230–303 K), a moderate decrease between the melting point and 500 K, and a somewhat slower decrease at higher temperatures. Our measurements may be compared with those of Cornell,<sup>2</sup> who measured  $T_1$  of  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  in liquid Ga over the more limited temperature range 275–475 K, and the measurements of Hanabusa and Bloembergen,<sup>6</sup> which extend from room temperature to 523 K. Our observed mea-

surements of  $T_1$  of  $^{71}\text{Ga}$  agree with those of the above authors, but our observed values of  $T_1$  of  $^{69}\text{Ga}$  disagree. In both cases our observed  $T_1$  of  $^{69}\text{Ga}$  is larger than theirs. Finally, our results may be compared to the recent measurements of Cartledge *et al.*<sup>9</sup> over the range 300–500 K. Our measured relaxation rates are slightly higher at 300 K but this difference increases with temperature and is outside the range of experimental error at 500 K. A discussion of these discrepancies is given in Sec. III B.

## 2. Gallium antimonide

Our Knight-shift data for liquid GaSb are shown in Fig. 3 together with measurements of the resonance shift in the solid just below the melting point. Liquid measurements below the melting point were possible owing to supercooling. An obvious feature of these data is the appearance of a large positive  $K$  for both the Ga and Sb nuclei accompanying the transition from the semiconducting phase to the metallic phase at the melting point. The Knight shift changes abruptly at the transition temperature with no evidence of an intermediate value of the shift in partially melted samples. The measurements show that the shifts for  $^{69}\text{GaSb}$  and  $^{71}\text{GaSb}$  are equal and independent of temperature over the whole range. They are given by

$$K(^{69}\text{GaSb}) = K(^{71}\text{GaSb}) = (0.482 \pm 0.001)\%.$$

In contrast to the  $^{69}\text{GaSb}$  and  $^{71}\text{GaSb}$  shifts, there is a slight difference in magnitude of the Ga  $^{121}\text{Sb}$  and Ga  $^{123}\text{Sb}$  shifts throughout the whole temperature range. At the melting point the shifts for the Sb isotopes are

$$K(\text{Ga } ^{121}\text{Sb}) = (0.667 \pm 0.001)\%,$$

$$K(\text{Ga } ^{123}\text{Sb}) = (0.669 \pm 0.001)\%.$$

Although this difference is only on the order of the

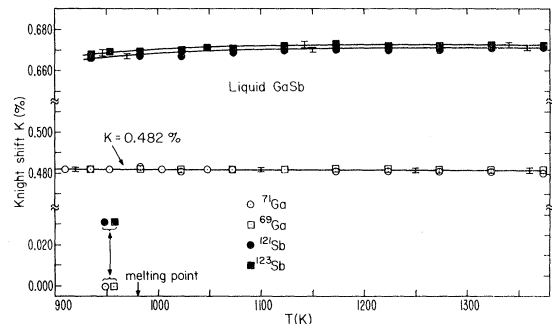


FIG. 3. Experimental Knight shifts  $K(^{69}\text{GaSb})$ ,  $K(^{71}\text{GaSb})$ ,  $K(\text{Ga } ^{121}\text{Sb})$ , and  $K(\text{Ga } ^{123}\text{Sb})$  for  $^{69}\text{Ga}$ ,  $^{71}\text{Ga}$ ,  $^{121}\text{Sb}$ , and  $^{123}\text{Sb}$  in liquid gallium antimonide as a function of temperature. Note the discontinuities in the vertical scale. The small shifts at 952 K were measured in solid gallium antimonide.

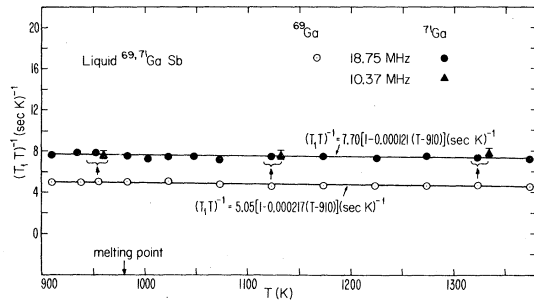


FIG. 4. Experimental values of  $(T_1 T)^{-1}$  for  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  in liquid gallium antimonide as a function of temperature. Data points within a given grouping were all taken at the temperature indicated by the corresponding arrow. The solid lines are the empirical fits to the data.

experimental error, the fact that it appears consistently throughout the entire temperature range leads us to believe that the difference is real. At one temperature (1123 K) a very careful measurement was made which showed the difference to be about five times the experimental uncertainty. The difference is almost certainly due to the hyperfine anomaly<sup>27</sup> of  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$ . This point will be discussed later in Sec. III C. A second characteristic of the data is the weak temperature dependence of the Ga  $^{121}\text{Sb}$  and Ga  $^{123}\text{Sb}$  shifts. The shifts slowly increase with temperature up to about 1160 K and then become independent of temperature over the rest of the range. The  $^{69}\text{Ga}$ ,  $^{71}\text{Ga}$ , and  $^{121}\text{Sb}$  data in Fig. 3 were obtained at an NMR frequency of 18.75 MHz, and the  $^{123}\text{Sb}$  data were obtained at 10.37 MHz.

The transition from a solid semiconductor to a liquid metal is reflected in the observed values of  $T_1$  as well as  $K$ . For example,  $(T_1)_{71}^{-1}$  increases by the factor  $135 \pm 9$  on going from the solid to the liquid state. Similarly,  $(T_1)_{69}^{-1}$  increases by  $47 \pm 3$ ,  $(T_1)_{121}^{-1}$  by  $65 \pm 4$ , and finally  $(T_1)_{123}^{-1}$  by  $48 \pm 3$  through the transition. The  $T_1$  data for liquid  $^{69,71}\text{GaSb}$  are plotted as  $(T_1 T)^{-1}$  versus temperature in Fig. 4. We note that  $(T_1 T)^{-1}$  decreases very slowly for both the  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  isotopes. The temperature dependences are described by terms linear in the temperature in the following empirical representations:

$$(T_1 T)_{71}^{-1} = (7.7 \pm 0.2)[1 - 0.000121(T - 910)] (\text{sec K})^{-1}$$

and

$$(T_1 T)_{69}^{-1} = (5.05 \pm 0.10)[1 - 0.000217(T - 910)] (\text{sec K})^{-1}.$$

The linear representations are valid with experimental error from 910 K (supercooled liquid) to 1373 K. The data were taken at 18.75 MHz for  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  and at several points throughout the

temperature range at 10.37 MHz for  $^{71}\text{Ga}$ . The observed relaxation rates were found to be independent of frequency over the entire temperature range for  $^{71}\text{Ga}$ .

The  $T_1$  data for liquid Ga  $^{121,123}\text{Sb}$  are plotted as  $(T_1 T)^{-1}$  versus temperature in Fig. 5. In contrast to the very slow variation of  $(T_1 T)_{69}^{-1}$  and  $(T_1 T)_{71}^{-1}$ , the  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$  data exhibit a gradual decrease of  $(T_1 T)^{-1}$  with increasing temperature between the supercooled region and 1100 K and a somewhat slower decrease at higher temperatures. The measurements of the  $^{121}\text{Sb}$  data were taken at an NMR frequency of 18.75 MHz and the  $^{123}\text{Sb}$  data were taken at 10.37 MHz. Also, at several points throughout the temperature range,  $(T_1 T)_{123}^{-1}$  was measured at 5.15 MHz; no frequency dependence was found.

### III. INTERPRETATION

#### A. Theory

Most of our experimental results will be discussed in terms of established theoretical models. Since these topics have been discussed at length elsewhere,<sup>17</sup> only a brief statement of the relevant formulas will be given here.

##### 1. Knight shift

There are three mechanisms which may make important contributions to the Knight shift in our experiments. The first ( $K_s$ ) is due to the contact hyperfine interaction. It is given by<sup>28</sup>

$$K_s = \frac{8}{3} \pi \chi_s \Omega \langle |u_F(0)|^2 \rangle, \quad (1)$$

where  $\chi_s$  is the spin susceptibility per unit volume for the  $s$  electrons,  $\Omega$  is the atomic volume, and  $\langle |u_F(0)|^2 \rangle$  is the average density at the nucleus of  $s$ -like Fermi-surface electrons. In addition there may be contributions from the orbital hyperfine interaction<sup>29</sup> ( $K_0$ ) and core polarization<sup>30</sup> ( $K_{cp}$ ).

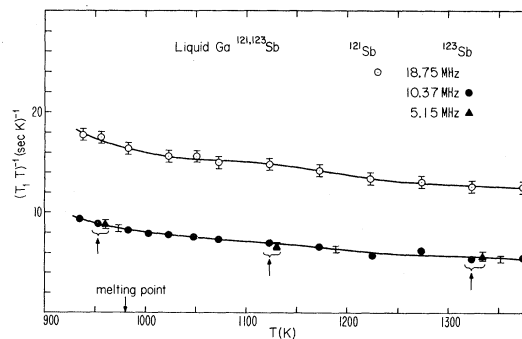


FIG. 5. Experimental values of  $(T_1 T)^{-1}$  for  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$  in liquid gallium antimonide as a function of temperature. Data points within a given grouping were all taken at the temperature indicated by the corresponding arrow. The solid lines are our fit to the data.

## 2. Spin-lattice relaxation

Spin-lattice relaxation can be caused by both magnetic and quadrupolar interactions. In the work reported here, measurements were made on two isotopes, thereby permitting separation of the observed rate into its magnetic and quadrupolar parts.<sup>31</sup> For this purpose we have used Eq. (7) and the symbols of Ref. 17. [Note that the third line of Eq. (7) should read  $W_Q^A = (W_A - R_M W_B) / (1 - R_M/R_Q)$ .]

In our experiments the dominant magnetic relaxation rate is seen to be due to the contact hyperfine interaction. This relaxation rate is given by<sup>32</sup>

$$W_M = \frac{64}{9} \pi^3 \hbar^3 \gamma_e^2 \gamma_n^2 \langle |u_F(0)|^2 \rangle N^2(E_F) kT, \quad (2)$$

where  $N(E_F)$  is the density of states at the Fermi surface for  $s$  electrons,  $\gamma_e$  is the electronic gyromagnetic ratio,  $\gamma_n$  is the nuclear gyromagnetic ratio and  $k$  is Boltzmann's constant. It is related to  $K_s$  of Eq. (1) by the modified Korringa relation<sup>33</sup>

$$T_1 T K_s^2 = \left( \frac{\hbar}{4\pi k} \right) \left( \frac{\gamma_e}{\gamma_n} \right)^2 \frac{1}{K(\alpha)}. \quad (3)$$

The correction factor  $K(\alpha)$  accounts for the effects of electron correlation and exchange on the Knight shift and relaxation rate. Other magnetic contributions are possible through orbital and dipolar interactions,<sup>34,35</sup> and by way of core polarization.<sup>36</sup>

Now we consider the quadrupolar contributions to the relaxation rate. The principal contribution in liquid metals is the thermal modulation of the charge distribution around a nucleus by diffusional and vibrational motion. Several authors have calculated the contribution to  $W_Q$  from diffusion motion in liquid metals. In the works of Borsa and Rigamonti,<sup>12</sup> Sholl,<sup>11</sup> Rossini *et al.*,<sup>3</sup> and Jolly and Titman,<sup>8</sup> the dominant part of the quadrupolar relaxation rate is given by

$$W_Q \propto \rho/D, \quad (4)$$

where  $\rho$  is the density and  $D$  the diffusion coefficient. The importance of vibrational motions for quadrupolar relaxation in liquid metals has been shown by Warren and Wernick.<sup>37</sup>

Finally, we note that direct quadrupolar relaxation in metals by conduction electrons has been proposed by Mitchell<sup>35</sup> and discussed by others.<sup>5,38,39</sup> In an earlier work<sup>17</sup> it was speculated that the disagreements between experiments and predictions of the diffusion model suggested that the direct relaxation process might be more important than commonly thought. For example, Rossini and Knight<sup>5</sup> estimated this mechanism to be capable of providing less than 1% of the observed  $W_Q$  in Ga and Sb.

It appears to us that there is essentially no possibility that the direct mechanism can compete with

diffusion as a mechanism for quadrupolar relaxation in liquid metals. This can be seen from the following rough estimate. In the case of diffusion, relaxation is caused via the diffusion of ion cores in a sea of electrons. The magnitude of the fluctuating electric field gradient will be about that of one screened electronic charge at the distance of the interatomic separation. The time scale for fluctuations is the diffusion jump time  $\tau_D$ . In the case of direct relaxation, the fluctuations come from the decay of an electronic wave packet located about an interatomic separation from the nucleus. If we neglect degeneracy effects, the magnitude of the fluctuating field gradient will be on the order of that from one screened charge separated by the interatomic spacing. But it is easily shown that the appropriate correlation time ( $\tau_F$ ) is the time it takes for an electron moving with the Fermi velocity to travel the interatomic spacing.<sup>40</sup> In the short-correlation-time limit appropriate for liquid metals, the relaxation rate is proportional to the square of the interaction strength multiplied by the correlation time.<sup>40</sup> From the above estimates it is seen that the two processes will have comparable interaction strengths. On the other hand, for liquid metals,  $\tau_D \sim 10^{-12}$  sec and  $\tau_F \sim 10^{-16}$  sec. Hence, the rough expectation is that the direct process has a rate on the order of  $10^{-4}$  that of the diffusion process because its correlation time is so much shorter. The inclusion of electron degeneracy would be expected to make the difference in rates even larger.<sup>40</sup> It therefore appears unlikely that the Mitchell mechanism has any chance of competing with diffusion as an important mechanism for quadrupolar relaxation in liquid metals.

## B. Gallium

The discussion of our results for Ga will be separated into two parts: magnetic interactions and quadrupolar interactions.

### 1. Magnetic interactions

The effects of fusion on  $K$  and  $T_1$  in metallic Ga can be considered because these quantities have also been measured in the solid. Measurements of the isotropic Knight shift by Valic<sup>18</sup> in solid Ga from 4.2 to 300 K give

$$K_{\text{iso}}(^{71}\text{Ga})_{\text{solid}} = (0.132 \pm 0.004)\% \quad (4.2 \text{ K}),$$

$$K_{\text{iso}}(^{71}\text{Ga})_{\text{solid}} = (0.142 \pm 0.003)\% \quad (77 \text{ K}),$$

$$K_{\text{iso}}(^{71}\text{Ga})_{\text{solid}} = (0.155 \pm 0.004)\% \quad (300 \text{ K}),$$

whereas in the liquid phase we observe

$$K_{\text{iso}}(^{71}\text{Ga})_{\text{liq}} = (0.4528 \pm 0.0005)\% \quad (303 \text{ K}).$$

This large difference in  $K$  between the solid and liquid states is not surprising in view of the fact

that the magnetic spin-lattice relaxation rates in the solid as measured by Hammond, Wikner, and Kelly<sup>41</sup> are also much smaller than what would be expected on the basis of extrapolating the magnetic relaxation rates in the liquid to lower temperatures. These differences between the solid and the liquid undoubtedly reflect a significantly larger  $N(E_F)$  in the liquid than in the solid.

In spite of the large change in  $K_{iso}$  at the melting point, from the standpoint of magnetic resonance the magnetic interactions are rather close to the behavior of free electrons interacting with the nuclei via the contact hyperfine interaction. For the case of the solid, Valic<sup>18</sup> has made the appropriate analysis of experimental results and finds that the data over the entire temperature range can be fit by the enhancement factor  $K(\alpha) = 0.80 \pm 0.04$ . (The error is our assignment; it is based on the stated errors in  $T_1$  and  $K_{iso}$ .)

Next we consider the case of the liquid state. Since relaxation measurements have also been made for both isotopes in this case, we can decompose the observed rates into magnetic and quadrupolar rates using the known nuclear properties.<sup>31</sup> The results of this decomposition for our results are shown in Fig. 6. There it is seen that the magnetic interactions are considerably larger than the quadrupolar interactions except in the supercooled state for <sup>69</sup>Ga, where the relaxation rates become comparable. A similar decomposition has been done in the temperature ranges 300–525 and 275–475 K by Hanabusa and Bloembergen<sup>6</sup> and by Cornell,<sup>2</sup> respectively. In comparison, our accuracy is considerably higher than that of these authors and we have covered a much larger temperature range. Also, there appears to be a systematic difference

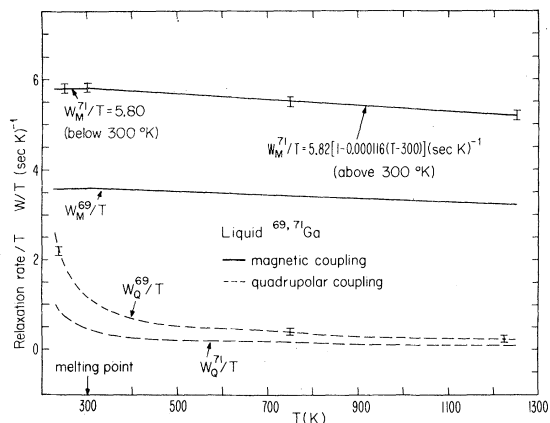


FIG. 6. Experimental (relaxation rate)/temperature as a function of temperature for magnetic and quadrupolar relaxation of <sup>69</sup>Ga and <sup>71</sup>Ga in liquid gallium. The rates were calculated from the method of Ref. 17 using experimental values represented by the "best-fit" solid lines in Fig. 2.

between our data and theirs (which will be discussed in Sec. IIB2). There is a discrepancy between our results and those of Cartledge *et al.*,<sup>9</sup> who have resolved their relaxation rates into magnetic and quadrupolar parts over the temperature range  $300 \leq T \leq 500$  K. Some discussion of this difference is given later in this paper. For the time being we shall proceed on the basis of our data.

Now we consider the changes which occur at the melting point. By using the observed values of  $K$  and  $W_M$  (total magnetic relaxation rate), we obtain a value of the correction factor in the liquid at the melting point:

$$K(\alpha) = 0.80 \pm 0.02 \quad (303 \text{ K}).$$

It is seen that within experimental error the observed value of  $K(\alpha)$  is the same in the solid and liquid phases. We will now discuss the significance of this equality. Recalling that there are several contributions to the Knight shift, we can write

$$K_{\text{expt}} = K_s + K_{\text{cp}} + K_0.$$

In the absence of a calculation for  $K_{\text{cp}}$  and with no experimental method of separating the three contributions, this expression can be condensed to  $K_{\text{expt}} = K_s + K_{\text{other}}$ . It is important to note the difference between the true  $K(\alpha)_{\text{true}}$ , which accounts for electron correlation and exchange and is given by the Korringa relation for  $s$  electrons, and the observed  $K(\alpha)_{\text{obs}}$  obtained from the Korringa relation using experimental data. The Korringa relation for  $s$  electrons can be written as

$$T_1 T K_s^2 = S / K(\alpha)_{\text{true}}.$$

The observed  $K(\alpha)$  is given by

$$T_1 T (K_s + K_{\text{other}})^2 = S / K(\alpha)_{\text{obs}}.$$

Solving these equations for  $K(\alpha)_{\text{true}}$  gives

$$K(\alpha)_{\text{true}} = K(\alpha)_{\text{obs}} (1 + K_{\text{other}}/K_s)^2.$$

Above, it was shown that  $K(\alpha)_{\text{obs}}$  is the same in the solid and liquid phases. This implies that  $K_{\text{other}}/K_s$  is the same in the solid and liquid states. This is an unexpected result in view of the conclusion of Valic<sup>18</sup> that the  $p$  character of the conduction electrons (which is responsible for  $K_{\text{other}}$ ) decreases by a factor of  $\sim 0.7$  upon melting. Valic's conclusion is reasonable because the complicated band structure disappears upon melting and so the  $p$  character in the wave function is considerably reduced. Our conclusion that  $K_{\text{other}}/K_s$  remains constant through melting assumes that there is no substantial change in  $K(\alpha)_{\text{true}}$  upon melting. But there is no evidence that  $K(\alpha)_{\text{true}}$  undergoes large changes through melting in liquid metals. It seems unlikely that a change in  $K(\alpha)_{\text{true}}$  would exactly cancel out a change in  $K_{\text{other}}/K_s$ .

Under the assumption that  $K(\alpha)_{\text{true}}$  does not

change through melting and the evidence that the  $p$  character of the conduction electrons decreases by a factor of  $\sim 0.7$  through melting without changing  $K_{\text{other}}$  it is reasonable to conclude that  $K_{\text{other}} \approx 0$  in the solid and liquid phases of Ga, and that the true  $K(\alpha)$  equals the observed  $K(\alpha) = 0.80$ . We therefore conclude that the dominant contribution (if not total) to  $K$  in liquid Ga is provided by the direct contact hyperfine interaction.

The reduction of  $\chi_s$  and  $\langle |u_F(0)|^2 \rangle$  responsible for the observed decrease of the Knight shift at higher temperatures should have a corresponding effect on the contribution of the magnetic contact interaction to the spin-lattice relaxation rate. From the Korringa relation [Eq. (3)] we find that  $T_1TK^2$  is constant over the temperature range 300–1250 K, and is equal to

$$T_1TK^2 = 3.53 \pm 0.07.$$

This gives a correction factor  $K(\alpha) = 0.80 \pm 0.02$ , which is further evidence that the contributions to  $K$  and  $T_1$  (magnetic part) in liquid Ga over the whole temperature range are purely the contact hyperfine interaction.

Now we turn to a discussion of the supercooled state of liquid Ga. Our measurements of  $K$  in the supercooled state agree with the findings of Suzuki and Uemura,<sup>25</sup> in which the negative temperature coefficient  $(\partial K/\partial T)_p$  decreases below the melting point in the supercooled state. Suzuki and Uemura suggest the possibility that this is due to a phase change in liquid Ga just below the melting point. They have also found that the magnetic susceptibility indicates a small diamagnetism which increases slightly with decreasing temperature. The bulk susceptibility of solid Ga has been measured and found to be  $-0.257 \times 10^{-6}$  cgs mass units for polycrystalline spheres at 25 °C and  $+0.003 \times 10^{-6}$  at 30 °C. Therefore, solid Ga is highly diamagnetic and the liquid weakly paramagnetic.

From Fig. 6 we see that the temperature dependence of  $(T_1T)^{-1}$  (magnetic part) in the supercooled state also decreases in slope and actually is temperature independent within experimental error. The enhancement factor  $K(\alpha)$  is found to be constant between 230 and 300 K within experimental error and equals  $0.80 \pm 0.02$ , which is the same result found in the liquid above the melting point and in the solid. From the available information there is little to show that there is a phase change in the supercooled state. Suzuki and Uemura found no discontinuities in measurements of electrical resistivity and density in going from the normal state to the supercooled state. In fact, their Figs. 11 and 12 show data which appear to fit a smooth curve about as well as two straight lines with differing slopes. Since  $K$  and the spin-lattice relaxation rate in the supercooled state are smaller than

the extrapolated values above the melting point, and since the magnetic susceptibility indicates a small diamagnetism which increases slightly with a decrease of temperature, it appears that the supercooled state tends to change its structure to more closely resemble the solid state. It is doubtful, however, that this reflects a phase change since changes of  $K$  and  $(T_1T)^{-1}$  with decreasing temperature are gradual and quite small. Also, x-ray-diffraction measurements between 273 and 323 K by Rodriguez and Pings<sup>42</sup> show that the structure of liquid Ga in the supercooled state does not differ significantly from that in the normal-liquid state. In addition, careful measurements of the liquid static structure factor by Chen<sup>43</sup> above and below the melting point show no evidence of a phase change. A similar phenomenon occurs in the case of In<sup>121,123</sup>Sb, where it is found that the magnetic relaxation rates decrease as the temperature is lowered into the supercooled state. Warren and Clark<sup>17</sup> attribute this to an increase of local order as the temperature is lowered below the melting point.

This section will be concluded with a discussion of the differences between our  $W_M$  measurements and those of other workers. In the case of Cornell,<sup>2</sup> and of Hanabusa and Bloembergen,<sup>6</sup> there is agreement within the experimental errors. The situation is different with Cartledge *et al.*<sup>9</sup> Over the common range  $300 \leq T \leq 500$  K, their measured rates are somewhat lower than ours. Upon resolution into magnetic and quadrupolar parts for <sup>69</sup>Ga there is essential agreement for  $W_Q$ , but our rates for  $W_M$  are somewhat larger than theirs, and more so at the high-temperature end of the range. Most such discrepancies in relaxation rates for liquid metals have been resolved by acceptance of the lower rate as more nearly correct and blaming the difference on impurities in the sample or some other sample-dependent effect. In this case, the correct interpretation is not so clear. If the measurements of Cartledge *et al.* are accepted, their values for  $W_M$  [ $= (1.52T + 523) \text{ sec}^{-1}$ ] with our values of  $K$  imply that  $K(\alpha)$  drops from 0.72 at 300 K to 0.59 at 500 K, as opposed to our temperature-independent value  $0.80 \pm 0.02$ . Such a large drop in the liquid state is rather unusual in a trivalent metal. For example, in liquid In,<sup>8,17</sup> and Al,<sup>44</sup> it is observed that  $K(\alpha)$  changes by a much smaller percentage over a wide temperature range in the liquid. As a result of these considerations we believe that the discrepancy in the values for  $W_M$  is unresolved.

## 2. Quadrupolar interactions

From the decomposition of the observed relaxation rates for <sup>69</sup>Ga and <sup>71</sup>Ga in liquid Ga, shown in Fig. 6, we see the temperature dependence of the

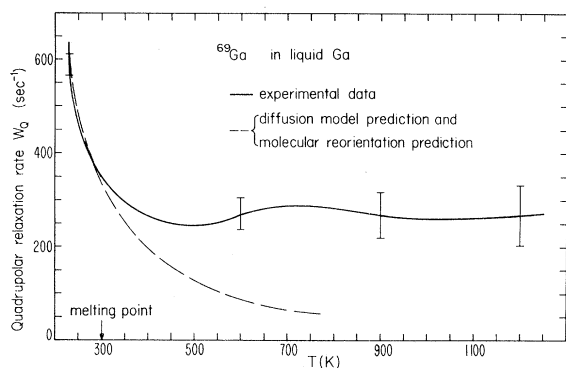


FIG. 7. Experimental quadrupolar relaxation rate as a function of temperature of  $^{69}\text{Ga}$  in liquid Ga. The predicted contributions to the quadrupolar relaxation rate of the diffusion model and molecular-reorientation model renormalized at the melting point are also shown.

quadrupolar relaxation rates plotted as  $(T_1T)^{-1}$  versus temperature. A plot of the quadrupolar relaxation rate  $W_Q$  versus temperature is shown in Fig. 7 for the case of  $^{69}\text{Ga}$  and reveals more clearly the surprising details of the temperature dependence. With an increase of temperature a very rapid decrease of  $W_Q$  in the supercooled state occurs which tends to level off at about 150 K above the melting point (450 K). Above this temperature  $W_Q$  begins to increase and maximizes around 730 K. At higher temperatures  $W_Q$  decreases again to a temperature-independent value which is approximately the same value of  $W_Q$  at 450 K. The mild peak in the resolution at 750 K is smaller than the indicated errors and probably should not be taken seriously.

Our results for  $W_Q$  in liquid Ga can be compared to the earlier results of Cornell<sup>2</sup> (275–475 K), Hanabusa and Bloembergen<sup>6</sup> (300–525 K), Cartledge *et al.*<sup>9</sup> (300–500 K), and Riegel *et al.*<sup>7</sup> (313–1323 K). Cornell's decomposition was not done in the most general way and has been recalculated by Rossini and Knight.<sup>5</sup> Their results show a slight increase of  $W_Q$  between 300 and 475 K, whereas our results show a definite decrease in this range. Also, Cornell's values for  $W_Q$  are approximately a factor of 2 larger than our values. There are several possible reasons for this discrepancy. First of all, our error bars are almost an order of magnitude smaller than those of Cornell's. Second, we found that  $W_Q$  below 600 K was very sensitive to sample history. Our preliminary measurements of  $W_Q$  near the melting point were approximately the same as Cornell's. However, after repeated cycling of the temperature up to 1250 K and back down, we found  $W_Q$  in the range 300–600 K to continually decrease. Above 600 K, no effects of sample history were measurable. After annealing the sample at  $\sim 1000$  K for several

days, we found that  $W_Q$  reached a minimum and thereafter was independent of temperature cycling. This extra contribution to the quadrupolar relaxation was probably due to diffusing impurities which tend to anneal out. A similar situation occurred in the case of solid Cu. Warren and Clark<sup>45</sup> found that  $(T_1)^{-1}$  in solid Cu at 1000 K decreased when the sample temperature was maintained above 1000 K for periods of the order of 24–48 h. The results of Hanabusa and Bloembergen also show  $W_Q$  near the melting point to be roughly a factor of 2 larger than our data. They find that  $W_Q$  decreases between 300–525 K, in agreement with our data, but their measured temperature dependence is larger than ours by about a factor of 2. The discrepancies are probably due to the existence of impurities left by insufficient sample annealing. As mentioned previously, our measurements of  $W_Q$  are in agreement with those of Cartledge *et al.* Finally we note the related work of Riegel *et al.*,<sup>7</sup> who used perturbed angular correlations to measure the relaxation rate of excited  $^{71}\text{Ge}$  in liquid Ga. They also separate the total rate into magnetic and quadrupolar parts. Since, however, only one isotope is observed, they are forced to use a theoretical approach to separate the magnetic and quadrupolar rates. Their use of a simple diffusion model and an assumed temperature independence for  $K(\alpha)$  leads to a temperature dependence of  $W_Q$  which is significantly different from our result. We believe that our results present the correct picture and that theirs suffer from having to work with only one isotope and make a separation based on a theoretical model. Their method does, however, appear to have one important advantage over conventional NMR methods. It can be employed over a much wider range of external magnetic fields and, hence, probe a much wider range of correlation times in the interactions responsible for nuclear relaxation.

It has already been proposed that the quadrupolar relaxation in Ga is due to diffusional motion of the ions in the liquid. The value of  $W_Q$  near the melting point was calculated to be  $840 \text{ sec}^{-1}$  by Borsa and Rigamonti<sup>12</sup> and  $500 \text{ sec}^{-1}$  by Sholl.<sup>11</sup> These do not compare well with our value of  $354 \text{ sec}^{-1}$  at the melting point. Recently Warren<sup>13</sup> has calculated this rate using a new theory which incorporates measurements of the liquid structure factor. His result is  $330 \text{ sec}^{-1}$ , which agrees very well with our observed value.

Since many workers have proposed that quadrupolar relaxation in liquid metals is due to simple diffusion jumps, we now indicate the relationship of our results to such theories. Those of Borsa and Rigamonti and Sholl predict a temperature dependence  $W_Q \propto \rho/D$ . A plot of  $W_Q \propto \rho/D$  normalized to the measured value of  $W_Q$  at the melting



point is shown in Fig. 7. Values for  $D$  are from the work of Broome and Walls.<sup>46</sup> The very small change in  $\rho$  has been neglected. The agreement with experiment is quite good in the supercooled region but becomes increasingly poor at higher temperatures. For the case of liquid In, Rossini *et al.*<sup>3</sup> have calculated separately the contributions to  $W_Q$  from diffusing ionic charges (neglecting conduction-electron effects) and from modulation of the  $p$ -conduction-electron charge distribution (treated as covalent bonds) by thermal motion. They conclude that the latter effect was definitely the most important. It is known from x-ray studies<sup>47</sup> that the crystal structure of solid Ga consists of pairs of ions in the lattice, in which a single nearest neighbor is found significantly closer than the three neighboring pairs. X-ray studies<sup>42</sup> in liquid Ga from 0 to 50 °C also suggest that there is a nearest neighbor at about 2.5 Å, which indicates a Ga-Ga complex in the liquid as in the crystal. Positron-annihilation experiments<sup>48,49</sup> in liquid Ga have shown anomalous behavior which also indicates the possibility of Ga pairs, but so far there is no definite proof. Finally, from neutron-diffraction studies Ascarelli<sup>50</sup> suggests that the structure of liquid Ga, at least at temperatures not far from the melting point and on a short-range order scale, displays the main features of the structure of the metastable solid,  $\beta$  phase<sup>51</sup> (which melts at -16.3 °C). This phase exhibits a considerable degree of anisotropy.

The evidence of some form of Ga-Ga association would imply some form of  $p$ -type covalent bonding between ions. The contribution to  $W_Q$  from modulation of the  $p$ -conduction-electron distribution by ionic motion which Rossini *et al.* found so important for liquid In would therefore be very important in this case also. This may explain the good agreement of the temperature dependence of the experimental  $W_Q$  with the diffusion-theory prediction of  $W_Q \propto \rho/D$  in the region near the melting point.

Alternatively, Faber<sup>52</sup> discussed a molecular-rotation model in which there are  $\text{Ga}_2$  "molecules" in the liquid state and suggested that  $W_Q$  could be due to these  $\text{Ga}_2$  molecules in a state of free rotation. This would lead to a temperature dependence<sup>53</sup>

$$W_Q \propto \eta V/T, \quad (5)$$

where  $\eta$  is the viscosity,  $V$  is a representative volume of the molecule, and  $T$  is the temperature. Using the values of  $\eta$  from Spells,<sup>54</sup> a calculated plot of  $W_Q$  normalized at the melting point is shown in Fig. 7 assuming no dissociation. It is seen that the temperature dependence is that of the diffusion model. Also, one would expect molecular dissociation with higher temperatures and this would lead

to even greater disagreement with the experimental results.

The contributions from vibrational motion, as pointed out by Warren and Wernick,<sup>37</sup> which tend to increase the value of  $W_Q$  at higher temperatures, may bring the theory more in line with the experimental results. However, a quantitative discussion of the data is very difficult at this time because in a liquid metal one has the following three processes occurring simultaneously: (i) The liquid expands with  $T$  and hence the interaction of the ions decreases. (ii) The vibrational amplitudes increase with  $T$ , creating larger electric field gradients. (iii) Diffusion of ions causes temperature-dependent quadrupolar relaxation. Warren and Wernick have pointed out that for a proper analysis of  $W_Q$  for liquid metals one must consider the data from inelastic neutron scattering experiments in order to derive dynamical information, i.e., information on high-frequency collective oscillations. Elastic scattering experiments give information on average atomic positions, which are useful for diffusional relaxation calculations, but the contribution from vibrational modes cannot be seen in this way. Warren<sup>13</sup> has recently produced a new theoretical analysis of this problem which is applicable to liquid Ga, and which has promise as a satisfactory explanation for  $W_Q$ .

### C. Gallium antimonide

Since the direct contact contribution to  $K$  depends on the electronic susceptibility and the density of  $s$ -like conduction electrons at the nucleus, it is of interest to compare the shifts observed in liquid gallium antimonide with the values obtained in the pure liquid metals gallium and antimony. The Knight shift of Ga in GaSb [ $K(^{71}\text{GaSb})$ ] is 7% larger than  $K(^{71}\text{Ga})$  in liquid Ga, whereas the shift  $K(\text{Ga }^{121}\text{Sb})$  in liquid GaSb is 6% smaller than  $K(^{121}\text{Sb})$  in liquid Sb,<sup>17</sup> at the respective melting points. These qualitative features are reasonable since the average number of electrons per atom in GaSb is intermediate between the valence of gallium ( $Z=3$ ) and that of antimony ( $Z=5$ ). However, quantitative differences are difficult to explain because one has to take into consideration changes in the electronic  $s$  and  $p$  character of the wave functions at the Fermi surface.

Although the measured Knight shifts of  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  in GaSb are equal within experimental error over the whole temperature range, there is a small but consistent difference in  $K$  for  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$  in liquid GaSb. We believe that this difference is due to the hyperfine anomaly of  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$ . The Knight shift may be written as<sup>55</sup>

$$K = a(s) \chi_p \xi M / 2g_I \mu_B, \quad (6)$$

where  $a(s)$  is the hyperfine interaction between the

nucleus and the conduction electrons,  $\chi_p M$  is the average electronic susceptibility per atom,  $\xi$  is the ratio of the probability densities in the metal and the free atom, and  $g_I = \mu_I/I$ . It is generally assumed that  $a(s)$  arises from  $s$  electrons since the contact interaction for these will be particularly large.

The hyperfine interaction constant  $a$  is a measure of the strength of the interaction between the nuclear dipole moment  $\mu_I$  and the moment due to the orbital electron. For two isotopes (subscripts 1 and 2) of the same element in the same electronic state, one expects  $a_1/a_2 = g_1/g_2$  if there is no spatial extent to the nuclei. However, when the size and shape of the isotopes are taken into account, there can be a hyperfine anomaly<sup>27</sup>  $\Delta$ , where

$$\frac{a_1}{a_2} = \frac{g_1(1+\Delta)}{g_2} \quad (7)$$

The most important contribution to  $\Delta$  is the difference in the spatial distribution of magnetic moment within the isotopes.

It can readily be seen from Eqs. (6) and (7) that if the hyperfine interaction arises from  $s$  electrons only,  $\Delta = K_1/K_2 - 1$ . From a very careful measurement at 1123 K we find  $\Delta_{\text{expt}} = (-0.36 \pm 0.07)\%$ . This result may be compared to the earlier measurement of the hyperfine anomaly of  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$  in antimony-doped silicon by Eisinger and Feher,<sup>27</sup> who used the more accurate technique of electron-nuclear double resonance (ENDOR). They found that  $\Delta = (-0.352 \pm 0.005)\%$ . The agreement between our results and those of Eisinger and Feher shows that the electrons responsible for the Sb Knight shift and the hyperfine interaction in antimony-doped silicon have the same fractional  $s$  character. This is so because  $s$  electrons are the only ones which could contribute significantly to the hyperfine structure anomaly  $\Delta$ . The wave function of the donor electron in silicon has been calculated by Kohn and Luttinger<sup>56</sup> and is found to resemble a hydrogenic  $s$  state. Hence, we may conclude that the Knight shift of Sb in liquid GaSb is caused mainly by  $s$  electrons, i. e., at least 80% with the experimental accuracy here. This is so because an appreciable contribution to  $K$  in liquid Ga  $^{121,123}\text{Sb}$  from non- $s$  electrons would make  $\Delta_{\text{expt}}$  smaller<sup>57</sup> than the  $\Delta$  measured in antimony-doped silicon, where the electron wave function is a hydrogenic  $s$  state.

We now turn to the additional information available from the  $T_1$  data. First we consider the case of  $^{69,71}\text{Ga}$  in liquid GaSb. In the usual way<sup>17</sup> the observed rates are decomposed into magnetic and quadrupolar parts, as shown in Fig. 8. We see that almost all of the relaxation is of magnetic origin. Both of the contributions show a slow decrease with increasing temperature. Because the magnitude of  $W_Q$  is of the same order of the error,

it is not possible to make definite determinations of the true temperature dependence. We can compare these results to the case of pure Ga (Fig. 6). We see that for  $^{69,71}\text{GaSb}$ ,  $W_M$  is larger than  $W_M$  for pure Ga, which is consistent with the fact that the Knight shift of  $^{69,71}\text{GaSb}$  is also larger. In contrast, we find that  $W_Q$  of  $^{69,71}\text{GaSb}$  is the same within experimental error as for pure  $^{69,71}\text{Ga}$  over the same temperature range. The values of  $(T_1 T)^{-1}$  and  $K(^{69,71}\text{GaSb})$  decrease slowly with increasing temperature in such a way that the product  $T_1 T K^2$  is constant from the supercooled state to 1373 K. In this temperature range the correction factor  $K(\alpha) = 0.92 \pm 0.04$ . We note that  $K(\alpha)$  for Ga in liquid GaSb is larger than  $K(\alpha)$  of pure liquid Ga. However, some decrease of  $K(\alpha)$  might be expected to occur as the electron density increases with increasing Sb content.<sup>33</sup> This may be an indication that an appreciable negative core-polarization contribution to the Knight shift of Ga in liquid GaSb is present.

Now let us consider the data for the Sb isotopes. Again, using the decomposition procedure we find the magnetic and quadrupolar contributions as a function of temperature as shown in Fig. 9. In contrast to the  $^{69,71}\text{Ga}$  results, we see a large quadrupolar contribution for  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$  which decreases with increasing temperature. The observed values of  $W_M$  and  $K(\text{Ga}^{121,123}\text{Sb})$  increase slowly with temperature from the supercooled region to 1373 K. The corresponding correction factor  $K(\alpha)$  is found to increase from  $0.79 \pm 0.04$  to  $0.84 \pm 0.10$ . It is not easy to give a unique interpretation to these experimental results.

It should be noted that NMR experiments<sup>17</sup> in liquid InSb show evidence of a large change of struc-

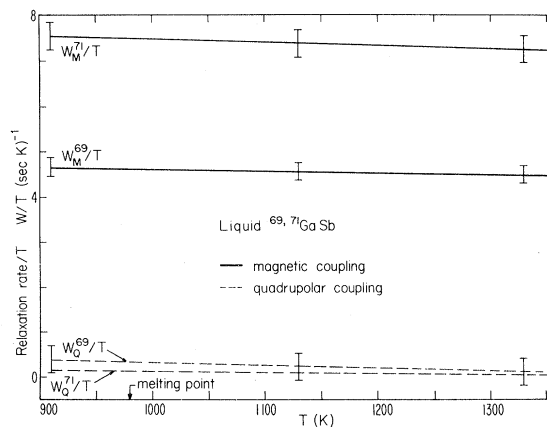


FIG. 8. Experimental (relaxation rate)/temperature as a function of temperature for magnetic and quadrupolar relaxation of  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  in liquid gallium antimonide. The rates were calculated from Ref. 17 using experimental  $T_1$  values represented by the best-fit solid lines in Fig. 4.

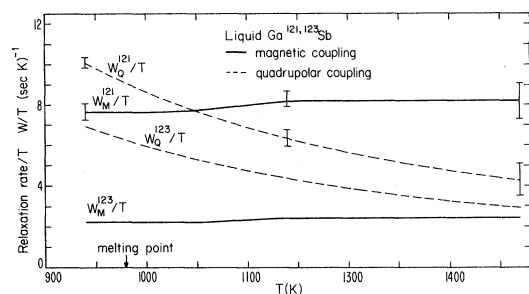


FIG. 9. Experimental (relaxation rate)/temperature as a function of temperature for magnetic and quadrupolar relaxation of  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$  in liquid gallium antimonide. The rates were calculated from Ref. 17 using experimental  $T_1$  values represented by best-fit solid lines in Fig. 5.

ture between  $\sim 760$  and  $1000$  K, and above this range the changes in electronic structure appear to be complete. On the other hand, liquid GaSb does not show evidence of any change of this magnitude. However, because of the higher melting point of GaSb, our data extend down to only  $940$  K. Above this temperature  $W_Q$  and  $W_M$  for Sb in InSb and GaSb are quite similar in temperature dependence and magnitude. Hence it appears that the degree of local order and the electronic structure of a liquid III-V compound may not depend on its melting point, but more so on the absolute temperature.

In order to identify the coupling mechanism responsible for the observed quadrupolar relaxation, it is important to compare the observed temperature dependence of  $W_Q$  with the predicted temperature dependence of the various theories. The ionic diffusion models of Borsa and Rigamonti and of Sholl both predict  $W_Q \propto \rho/D$ . The comparison of the observed temperature dependence with the predictions of these models could be accomplished easily if the self-diffusion coefficient were known at various temperatures since, in that case, one could calculate the expected temperature dependence and compare it directly with experiment. Unfortunately, self-diffusion measurements have not yet been reported for liquid GaSb. However, we shall estimate the temperature dependence of  $D$  from the available viscosity ( $\eta$ ) data<sup>58</sup> using the methods of Saxton and Sherby.<sup>59</sup> By assuming an Arrhenius form  $D = D_0 e^{-Q/RT}$  and the relationship  $\eta/T \propto D^{-1}$  we find  $Q/RT_M = 3.0 \pm 0.3$ , where  $T_M$  is the melting point. This agrees well with the empirical relation  $Q \sim 3RT_M$  of Saxton and Sherby,<sup>59</sup> which provides an adequate description of the experimental results for most liquid metals. On the other hand, if it is assumed that the experimental values of  $W_Q$  obey the temperature dependence  $W_Q \propto \rho/D$ , it is found that  $Q/RT_M = 1.6 \pm 0.3$ , suggesting a weaker temperature dependence than predicted by  $W_Q \propto \rho/D$ .

A similar difference occurs in the case of liquid antimony,<sup>17</sup> for which  $W_Q$  does not decrease as rapidly with increasing temperature as implied by the calculated value of the activation energy  $Q$ . Hence, we conclude that besides a diffusion contribution to  $W_Q$  there is a definite indication that additional relaxation processes enter. We have presented arguments for the existence of a vibrational-motion contribution<sup>37</sup> to  $W_Q$  for the case of liquid Ga. It is reasonable that these collective oscillations also exist in liquid GaSb. At the present time, it is not clear how one can unravel the various contributions to the temperature dependence of  $W_Q$  without reliable theoretical calculations based on inelastic neutron scattering data. Similarly, it is difficult to make estimates of the magnitude of the various contributions. Considering for the moment the diffusion theories, besides the lack of direct measurements on the magnitude of the diffusion constant, the antishielding factor  $\gamma_\infty$  for Sb in liquid GaSb is unknown. Sholl<sup>11</sup> was able to make estimates of  $\gamma_\infty$  from the measured quadrupole coupling in the solid determined by nuclear quadrupolar resonance for the cases of Ga and In. However, in the solid state GaSb is a semiconductor and hence is quite a different substance in the liquid and solid. It is therefore difficult to infer the liquid properties from the solid. Sholl has pointed out that the uncertainty in  $\gamma_\infty$  is often the limiting factor in interpreting the experimental results. Finally, the diffusion models assume a pure metal, the fact that GaSb is a liquid compound with different valences causes additional uncertainty in the analysis.

Now we compare the magnitudes of  $W_Q$  for Ga and Sb in liquid GaSb, and draw some conclusions regarding their antishielding factors. At the melting point, we find

$$W_Q(^{69}\text{Ga})/W_Q(^{121}\text{Sb}) = 0.04 \pm 0.03 .$$

On the other hand, if equal antishielding factors and identical environments are assumed,<sup>60</sup>

$$W_Q(^{69}\text{Ga})/W_Q(^{121}\text{Sb}) = 1.79 .$$

This suggests strongly that the efg (electric field gradient) at the  $^{121}\text{Sb}$  nucleus is approximately 7 times as large as the efg at the  $^{69}\text{Ga}$  nucleus. Since the environment that each nucleus sees is approximately the same, this difference in efg may be due to large differences in the antishielding factors. This same phenomenon occurs in the case of liquid InSb,<sup>17</sup> where the Sb nuclei exhibit a much larger  $W_Q$  than In, although in the solid the  $\gamma_\infty$  are estimated to be almost equal.<sup>17</sup> For the case of pure Ga and pure-Sb metals, Rossini and Knight<sup>5</sup> have estimated that  $1 - \gamma_\infty$  for  $^{69}\text{Ga}$  and  $^{121}\text{Sb}$  are very nearly the same. This leads us to believe that alloying may enhance  $\gamma_\infty$  of the Sb ions over  $\gamma_\infty$  of the Ga ions in the liquid compound.

A plausible explanation of this is as follows. In a theoretical consideration of disordered alloys in the tight-binding approximation, Stern<sup>61</sup> has shown that in contrast to pure metals, the electron states in alloys exhibit a charging effect, i. e., a different electronic charge is deposited on each constituent in the alloy for a given state. The amount of charging can depend on valence difference, concentration, and the parameter  $\delta_0$ , which is the ratio between the difference of the atomic energies of the atoms in the alloy and the width of the alloy band. Stern has shown that in certain limits practically all of the charge can concentrate on one type of atom or the other. An ion core in a pure metal is strongly screened by the conduction electrons, and so the charge distribution about it will be almost neutral. Charging is zero in pure metals because all of the atoms are the same.

If we now form an alloy, and assume the phenomenon of charging, the almost neutral or slightly positive charge distribution present in the pure metals can now pass to the case where the Ga charge configuration becomes more positive and the Sb charge configuration changes to a negative state. There is some evidence from other studies that this behavior is to be expected. Recently Bucher and Maita<sup>62</sup> reported an experimental study of electronegativity and crystal fields in intermetallic compounds. Their findings indicate that ligands with low electronegativities generally exhibit positive ligand charges, whereas ligands with high electronegativities have negative ones. By using the electronegativity values of Gordy and Thomas<sup>63</sup> for Ga (1.5) and Sb (1.8), the charging proposed above appears plausible. We must now consider what effect this has on the antishielding factors. From theoretical calculations of antishielding factors for a number of ions, Wilner and Das<sup>64</sup> have pointed out several important tendencies. They note a very sharp change in  $\gamma_\infty$  in passing from a singly positive charged ion to a singly negative charged ion. On the other hand, the change in  $\gamma_\infty$  in passing from a singly positive charged ion to a triply positive charged ion is relatively small. These results are understandable because a negative ion binds its outer electrons loosely and there is a great increase in deformability in passing from the positive to the singly charged negative ions. The positive singly charged ions, on the other hand, strongly bind their outer electrons, so large changes in deformability with the addition of more positive charges would not be expected.

The above points indicate that  $\gamma_\infty$  of the Ga ions would change little upon alloying and  $\gamma_\infty$  of the Sb ions would increase greatly. This would explain the large difference in electric field gradients seen by the <sup>69</sup>Ga and <sup>121</sup>Sb nuclei. Also, for a given temperature, our data show that  $W_Q$  for <sup>69</sup>Ga is the

same in the pure metal and in GaSb within experimental error. Finally,  $W_Q$  of <sup>121</sup>Sb is approximately a factor of 3 larger in Ga<sup>121</sup>Sb than  $W_Q$  in pure Sb. These results are also consistent with our model. It must be noted that the viscosity<sup>58</sup> of liquid GaSb at the 50-50 composition shows a marked increase over the values of pure Ga and pure Sb. Since the viscosity is closely connected to the diffusion coefficient,<sup>59</sup> this increase could also explain the larger value of  $W_Q$  in liquid GaSb. However, this should have the same effect on  $W_Q$  of the Ga nuclei, in contradiction to what is observed. Also, the composition dependence of the viscosity does not explain the large difference in electric field gradients seen by the Ga and Sb nuclei. Recently, from work on several liquid-alloy systems containing nuclei with substantial quadrupole moments, it has been suggested<sup>8,10,65</sup> that it is normal behavior for  $W_Q$  to peak near the (50-50)% composition. Heighway and Seymour<sup>65</sup> concluded that this behavior is due to a dependence of the electric field gradients on concentration and they presented a simple random substitutional model which gave roughly the correct concentration dependence of  $W_Q$ . As we have mentioned, charging is also concentration dependent and hence might also explain this concentration dependence of  $W_Q$ . Extensive theoretical calculations on the concentration dependence of charging in liquid alloys are necessary before the importance of this mechanism is known. It is, of course, possible that both mechanisms operate simultaneously.

#### IV. SUMMARY AND CONCLUSIONS

Measurements of the Knight shift and nuclear spin-lattice relaxation rate of <sup>69</sup>Ga and <sup>71</sup>Ga in liquid Ga, and <sup>69</sup>Ga, <sup>71</sup>Ga, <sup>121</sup>Sb, and <sup>123</sup>Sb in liquid GaSb are reported over temperatures ranging from the supercooled regions up to 1250-1373 K.

In liquid Ga, the observed relaxation rate is separated into its magnetic and quadrupolar components. The quantity  $T_1TK^2$  is found to be constant over the whole temperature range. It is concluded that the contact hyperfine interaction accounts for all of the observed Knight shift. In the supercooled regions,  $K$  and  $W_M$  are slightly smaller than the extrapolated values above the melting point. This is interpreted as an increase of local order tending toward the solid state but not a phase change. The ionic-diffusion models adequately predict the temperature dependence of  $W_Q$  in the supercooled region and slightly above the melting point, but at high temperatures these theories are inadequate.

In liquid GaSb, the hyperfine structure anomaly is measured from the Knight-shift data for <sup>121</sup>Sb and <sup>123</sup>Sb. It indicates a purely s-state contact interaction within the experimental error of  $\pm 20\%$ .

The observed relaxation rate of Ga in GaSb is separated into its magnetic and quadrupolar parts. It is found that almost all of the relaxation is magnetic in origin. The value of  $K(\alpha)$  for Ga in GaSb is found to be constant over the whole temperature range.

The observed relaxation rate of Sb in liquid GaSb is separated into its magnetic and quadrupolar parts. Near the melting point,  $W_M$  and  $W_Q$  are found to be comparable. It is found that the ionic diffusion models by themselves predict the wrong temperature dependence of  $W_Q$ . In the case of GaSb, there is evidence that alloying can significantly alter the antishielding factors. A plausible model

is presented which is qualitatively consistent with the experimental facts.

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